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U.S. Nuclear Regulatory Commission
ATTN: Mrs. Deborah A. DeMarco
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11545 Rockville Pike
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Washington, DC 20555

Subject: Courtesy Copy of: "Corrosion Testing in Organic Liquids"

Dear Mrs. DeMarco:

Please find enclosed a courtesy copy of a chapter entitled "Corrosion Testing in Organic Liquids" that is being submitted for publication in the second edition of the ASTM book on Corrosion Tests and Standards. It is co-authored by Sean Brossia and Dave Shifler (Naval Surface Warfare). The chapter describes differences encountered when conducting corrosion tests in non-aqueous environments and does not involve NRC work. This copy is being supplied to you for your information and no action is needed on your part. Please note this letter is reissued with correct distribution.

If you have any questions regarding this paper, please feel free to contact Sean Brossia at (210) 522-5797 or myself at (210) 522-5439.

Sincerely yours,



Budhi Sagar
Technical Director

BS:VJ:jg

Enclosure

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Organic Liquids

C. S. Brossia¹ and D.A. Shiffler²

DESCRIPTION OF ENVIRONMENT

Overview

Organic liquids are used in a wide variety of industrial applications. They can be characterized as liquids that consist of one or more carbon atoms joined to other atoms via covalent bonds. Common atoms included in organic molecules are hydrogen, oxygen, nitrogen, sulfur, and halogens. Both the rate and yield of certain reactions have been found to greatly increase when performed in organic liquids. Thus, they are widely used in the chemical process industry for synthesis. With the increase in the use of organic liquids, increases in observed corrosion problems associated with the exposure of materials to them have also occurred. In some cases, failures involve an unacceptably large loss of metal or degradation of material properties. However, in many other cases, the major issue is discoloration or degradation of the organic solution resulting from corrosion of the processing vessel, as the solution is the product of commercial interest. For example, many pharmaceuticals are synthesized in organic solutions in large vessels. For these applications, the corrosion resistance requirements for materials used are stringent. The introduction of metals into a product can lead to rapid degradation of the product as well as health and safety concerns.

While corrosion in pure organic liquids can occur, many corrosion problems in organic liquids involve solutions with multiple components. For example, a solution containing ethanol, water, oxygen, and hydrogen chloride (HCl) contains four components. Some of the components may be present at small concentrations, but have dramatic effects. This is often the case with water due to its low molecular mass compared to many organic liquids. Small mass percentages of water can represent significant concentrations in moles/litre. For example, 100 ppm water in acetonitrile results in a water concentration of over 4 mM.

Organic liquids are classified in a variety of ways. A common classification scheme is based on the nature of the bonding between molecules during solvation. Three general categories exist: protic liquids, nonpolar aprotic liquids, and dipolar aprotic liquids. Protic liquids (e.g., alcohols, carboxylic acids, amines, amides) are those that can provide protons to other molecules. Solvation in protic organic solvents occurs through dipole-dipole interaction, ion-dipole interaction, and hydrogen bonding. These are generally miscible with water (another protic liquid) and can solvate both organic and inorganic acids. Nonpolar, aprotic liquid molecules (e.g., aromatic and aliphatic hydrocarbons) interact through weak van der Waals bonds and have little solvating ability. The protons in these liquids do not dissociate to any measurable extent. Dipolar, aprotic liquid molecules (e.g., acetonitrile, aldehydes, esters, ethers, dimethyl sulphoxide, tetrahydrofuran, dimethylformamide) interact via ion-dipole and dipole-dipole forces and usually strongly solvate cations and tend to be poor acceptors of electrons and poorly solvate anions in solution. Organic solvents may also have functional groups that are either hydrophobic, which repel water molecules, or hydrophilic, where the functional groups readily react with water. It has been shown

that the predominate interaction of a metal with an organic adsorbate is through its functional groups [1].

The wide variety of organic liquids leads to complexity in the analysis of corrosion problems. In addition, the large number of different liquids leads to difficulties due to the limited physical and chemical data on specific liquids. This has ramifications both for the recording of corrosion data, and for the development of a broad-based understanding of the important corrosion processes. The lack of physical and chemical information is a limiting factor in any broad description of behavior such as found in this chapter. Also, while many testing considerations can be generalized for organic liquids, the corrosion behavior of materials in nonaqueous solvents is not nearly as well understood as in aqueous solutions.

Types of Corrosion

The types of corrosion (i.e., the morphology of attack and the oxidation process) that can be encountered in organic liquids are the same as those observed in aqueous solutions. The solution chemistry and solution electrochemistry may be different, but the types of fundamental corrosion processes that occur remain the same. An excellent review of examples of corrosion in various organic solutions can be found in the work of Heitz [2]. In addition to a review of the fundamental principles involved, Heitz critically evaluates the literature published before 1973 and describes a number of industrial case histories of component failures due to corrosion in organic solutions. Kelly and Moran [3] summarized much of the work in aprotic liquids and put forth a general description of the effect of water on passivation processes.

Limits on Coverage of Section

Due to the wide variety of organic liquids, specific information relevant to each one cannot be covered in limited space. The focus of this chapter will be primarily on corrosion of metals in liquid phase, though many of the comments are applicable to nonmetals as well as vapor phase attack. Since corrosion in organic liquids is not fundamentally different than corrosion in aqueous solution, testing procedures for types of corrosion are generally very similar. Thus, only unique considerations with respect to testing in organic liquids will be considered.

Variables that Affect Corrosion

Since corrosion in organic liquids is not fundamentally different from corrosion in aqueous solutions, all of the variables that affect corrosion in aqueous solutions can affect corrosion in organic solutions. These include temperature, redox potential, presence and concentration of salts, acids and bases, and fluid velocity. However, there are a number of variables which are not possible in aqueous solution that can be important in organic solutions. The most important of these will be covered in the next section.

ASPECTS MAKING TESTING UNIQUE

There are several aspects to conducting electrochemical tests in organic liquids that are often not encountered or important while testing in aqueous solutions. These include effects due to low solution conductivities, the importance of the water concentration in the solution, the existence of an extremely wide variety of liquid compositions, the complexity of products from electroactive organic liquids, and a lack of thermodynamic data.

The low conductivity associated with most organic liquids can give rise to experimental problems with conducting electrochemical experiments. During electrochemical experiments in which a current is applied, the potential measured is the sum of the actual potential difference between the working and the reference electrodes plus the ohmic potential developed in the solution due to the passage of current through the solution which exhibits a finite resistance. This ohmic potential is also known as IR_s , where I is the current passing, and R_s is the solution resistance between the reference electrode and the working electrode. The conductivity of organic liquids is often less than that of pure water [4] as shown in Fig. 1. The resulting high solution resistance can result in the development of large ohmic potentials during the passage of even small currents. These ohmic potentials reduce the amount of the applied potential at the metal/solution interface and can affect the current/potential distribution on an electrode. Since the amount of the error changes as the applied current changes, a distorted current-potential relationship can result. More information on ohmic drop and ways to minimize or compensate for its effects can be found in the chapter on Electrochemical Tests in this manual [5]. One common method used to minimize ohmic drop in organic liquids is to add a supporting electrolyte. The ideal supporting electrolyte is a substance that substantially increases the conductivity of the solution without affecting the reactions that occur. However, since organic liquids do not solvate many salts in high concentrations, often only a small amount of supporting electrolyte can be added prior to reaching saturation. Supporting electrolytes are discussed in more detail below in the section on Important Experimental Variables.

Water concentration in organic liquids is difficult to control and measure at low levels. However, even small amounts of water can have dramatic effects on the corrosion behavior as shown in Table 1. In this case, the corrosion rate of aluminum decreases by 3 orders of magnitude due to a 0.3 mass % increase in the water concentration. Thus, even though each acid would be considered commercially pure, dramatic differences in corrosion rate due to small water additions are observed. This can also be true for other impurities that are often present in organic liquids. Thus, the measurement and control of water levels can be a key aspect to corrosion testing in organic liquids.

A popular technique to measure water content is the Karl Fischer Titration method [6]. This method can reliably analyze water contents as low as 100 ppm (0.01 mass %). Aliquots of solution can be taken before, during, and after an experiment to follow any changes in water content. Such changes can occur due to the tendency of some organics to absorb water from the ambient atmosphere. For example, it has been found that the water content of a 100 mL sample of methanol, exposed to laboratory air at 25°C with a relative humidity of approximately 55%, increased from 0.035 mass % to 0.42 mass % in 2 h as shown in Fig. 2 [7]. This illustrates the need for incorporating a sealed experimental cell or a dry glove box when working at low water levels. By

using one or both of these, water absorption can be minimized and water levels of 100 ppm and below can be realized in the pure liquid. Care must be taken when adding other components to the anhydrous liquid, as most salts as well as electrodes can add appreciable amounts of water to the solution which is then very difficult to remove. Also, extremely dry solutions can sometimes pose a safety hazard if suddenly exposed to air or water.

Organic liquids encompass an extremely wide variety of compounds. However, they can be classified into two main categories: aprotic (which are generally water insoluble) and protic (which are generally water soluble). Many solution properties such as solvating power, depend on the primary functional groups of the organic liquid. Thus, the protic nature of a given organic liquid will determine the solubility of various impurities and corrosion products. Even within a type of organic liquid, important differences emerge among individual liquids. For example, the corrosion rate of iron decreases in monocarboxylic acids as the chain length increases (Fig. 3) [2]. These differences among similar organic liquids adds another layer of complexity to the corrosion phenomena as compared to aqueous solution.

Related to liquid composition effects are cosolvent interactions. In many applications, a mixture of liquids (organic/organic, organic/inorganic) is of interest. Several aspects need to be considered when testing in such organic liquid mixtures which are not considered in aqueous solutions. First, there exists the possibility that when two or more liquids are combined they are either immiscible or have limited miscibility. This results in the formation of multiple liquid phases (phase separation) where the properties of each phase could be significantly different from others. The net result is that testing in mixtures can be difficult. The difficulty arises in trying to determine which phase or composition is detrimental to material behavior and may also involve partitioning of dissolved species between the various phases present. The possibility also exists that it is not an individual phase, but rather the interface between two phases in solution that is deleterious. Multiphase solutions cause special problems such as concentration of aggressive species into one phase (e.g., HCl into the aqueous phase of a HCl/water/dioxane mixture) [2], specific adsorption of one phase at the metal surface, and preferential attack at the phase boundary (akin to water line attack). Additional discussion of multiphase attack is outside the scope of this document, but can be found in Heitz's review [2].

One important manifestation of the large variety of organic liquids is the paucity of thermodynamic data. Thus, no equivalent to Pourbaix diagrams [8], used widely in aqueous solution, has been developed for any organic liquid. In fact, pH in organic liquids is not relevant in aprotic organic solvents since there is no readily available hydrogen. However, in nonaqueous solutions, it is possible to generate more powerful proton donors than the hydronium ion found in aqueous solutions. The strength of extremely strong acids in nonaqueous solution is measured by the Hammett acidity function which is defined for the reaction $B + H^+ \leftrightarrow BH^+$ [9]:

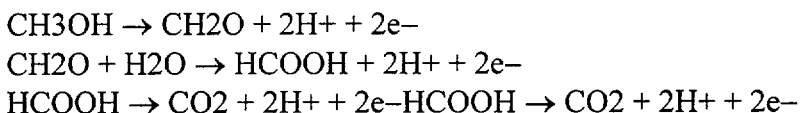
$$H_o = pK_{BH^+} - \log ([BH^+]/[B])$$

No standard metal/solution potential difference has been defined for all liquids. Some of the behavior in organic liquids can be explained by using the concept of Lewis acids and bases employed in the aqueous chemistry. A Lewis acid is an electron pair acceptor while Lewis base is

an electron pair donor. All the usual ligands can be considered Lewis bases and metal ions as Lewis acids.

In general, thermodynamic data in the literature pertaining to specific material/aqueous solution systems (e.g., Pourbaix diagrams) may not necessarily be valid for the same material in organic liquids. Some efforts have been made to develop electromotive series in different liquids as shown in Fig. 4. The reference point is given by the ferrocene/ferricinium⁺ couple. The selection of a reference electrode is discussed in a later section in this chapter. In general, the order of reversible potentials is maintained from aqueous solution, though the numerical values can change appreciably.

Finally, as is the case for water, organic liquids have a limited range of electrochemical stability. The products of these reactions are often also electroactive and can become involved in electrochemical or chemical reactions of interest. While solution oxidation or reduction can also occur in aqueous solutions, the products are simple bases or acids (i.e., H⁺ and OH⁻). However, the products resulting from electroactive liquids are usually a mixture of complex organic acids. These complex organic acids can combine with other ions in solution and form other chemicals that could be even more aggressive than the acid from which they were derived. This has been shown to be an issue in methanol by Smialowska [10] who found that galvanostatic polarization of stainless steel in pure methanol resulted in the formation of formic acid as follows:



The observed oxidation current was a mixture of metal dissolution and methanol oxidation, complicating comparisons of material loss and charge passed based upon Faraday's Second Law.

IMPORTANT ENVIRONMENTAL VARIABLES

The environmental variables that influence corrosion testing in organic liquids include metal, alloy or nonmetallic material in contact with the organic solution, solution conductivity, solution acidity, water content of the solution, presence and stability of oxide or other pre-existing films, type and concentration of surface contaminants or inclusions, functional group and concentration of organic solvent, solvent oxidation or reduction products, type and concentration of supporting electrolyte, applied potential, possible mechanistic paths for passivation, and temperature. As in all corrosion testing, matching the test environment to the actual service environment is critical for obtaining useful information. In addition, by studying the effects of these variables on the corrosion processes, better insights into the controlling mechanisms, as well as the sensitivity of the corrosion processes to changes in the service environment, can be gained.

As mentioned above, the high resistances often associated with organic solutions can distort electrochemical measurements. To minimize these ohmic losses, supporting electrolytes are often used. Ideally, supporting electrolytes dissociate and increase the solution conductivity without altering the corrosion process under study. A commonly used electrolyte is lithium perchlorate

(LiClO₄) in concentrations ranging from 10⁻² to 5 × 10⁻¹ mol/L. The perchlorate anion is thought to be inert in most solutions, and very weakly adsorbing to surfaces. Thus, LiClO₄ is not expected to affect the electrochemical reactions considered in most organic liquids. The addition of 0.1 M lithium perchlorate as a supporting electrolyte to methanol can increase the conductivity from 10⁻⁶ S/cm [4] to 6 × 10⁻³ S/cm, thereby reducing the ohmic resistance by a factor of 200. This reduction allows the experimenter to more easily compensate for the ohmic drop. For fundamental studies of corrosion in organic liquids, the addition of a well-chosen supporting electrolyte is a reasonable approach to allow electrochemical information to be gathered. For more applied measurements, the addition should be carefully considered and comparison tests (e.g., coupon exposures) should be performed to verify the absence of an effect of the supporting electrolyte on the corrosion process. If a supporting electrolyte is not added, caution must be used in the gathering and interpretation of electrochemical data. In some cases, where a supporting electrolyte cannot be added and the solution resistance is very high, the performance of meaningful electrochemical measurements is extremely difficult.

Acids have often been used as supporting electrolytes [4]. Strong acids (e.g., H₂SO₄, HCl, HNO₃) generally enhance the conductivity of organic solutions greatly. However, some organics are susceptible to degradation in acids. When water is present, acid hydrolysis becomes an additional degradation pathway [11]. Also, the acidity of the solution can have a controlling effect on the corrosion behavior of metals in organic solutions. For example, a recent review [3] of the literature on the corrosion of metals in aprotic liquids has shown that corrosion behavior, and more specifically, the mechanisms of passivity, are affected by the acidity of the solution. The mechanisms of passivation were classified into four types: (1) air-formed film, (2) salt film, (3) chemisorption of the liquid, and (4) oxide/oxyhydroxide formation. Acidity is deleterious to all four passivation mechanisms in organic solutions. Hence, control of acidity is important. In addition to H⁺, acidity also implies the presence of a corresponding anion. Its presence can alter material behavior by adsorbing to the surface in addition to increasing the solution conductivity. Thus, acids should not be considered as supporting electrolytes since they influence the behavior observed, unless the service environment contains acids, in which case they should be included in the test solution. An additional passivation mechanism has been proposed by Shifler et al. involving the formation of a passive electropolymerized film (polymer films in which the polymerization process is electrochemically activated) on bare steel surfaces in dimethoxyethane(DME)/LiAsF₆ solutions at potentials above the oxidation potential of DME [12]. The complex electropolymerization mechanism for carbon steel in dimethoxyethane/propylene carbonate mixtures with LiAsF₆ as the supporting electrolyte is dependent on: (1) DME concentration, (2) cationic intermediate adsorbed concentration and degree of coverage, (3) LiAsF₆ concentration, (4) applied potential, (5) rate of iron cation dissolution, and (6) water concentration. Decreases in any of these factors will either decrease the rate of electropolymerization or may prevent electropolymerization entirely [13]. Numerous other investigators have also examined the role of electropolymerized films as a means of metal passivation in dioxolane [14,15], ether [16-19], pyrrole [20,21], and carbazoles/dicarbazoles with polyether chain substitution [22], and phenol [23].

The supporting electrolyte may also play an integral role in passivation processes. In supporting electrolytes, increasing the size of the counter-ions may lead to a decreased film mobility and polyvalent ions, acting as stronger acids, may enhance the formation of crosslinks between chains and electrolyzed films [24]. It has also been observed that AsF₆⁻, added as a

supporting electrolyte, can be an integral component of the polymerization process on iron [19] and carbon steel [12] in DME; the use of either tetrabutylammonium perchlorate (TBAP) or lithium perchlorate as supporting electrolytes leads to alloy breakdown around the solvent oxidation potential [25]. The oxidation of aluminum was found to be influenced by the nature of the passivation mechanisms in nonaqueous solutions which depended on the kind of electrolyte salt [26].

The water concentration in the experimental testing solution should duplicate as accurately as possible the water concentration found in the actual service solution. This is because the concentration of water present in the testing environment affects material behavior and the solvating ability of the solution. The presence of water in minimal concentrations (0.1 to 0.5 mass %) in acidified protic organic liquid solutions leads to the passivation of several materials. For example, iron, stainless steel, and nickel exhibit this behavior in methanol [27-29] as shown in Fig. 5. Water concentrations outside this range generally lead to increased corrosion rates [28,29]. In neutral aprotic organic solutions, water in any concentration, except in high concentrations (i.e., 80+ mass %), tends to be deleterious. For example, iron and nickel in neutral dimethylsulfoxide were passive only when the water content was low (0.02 mass % for iron and 0.01 mass % for nickel) [30,31]. Iron in neutral propylene carbonate solutions exhibits similar behavior [32,33] as shown in Fig. 6. For other materials and liquids, for example molybdenum and chromium in methanol and dimethylformamide, and iron in acidified dimethylformamide, no clear dependence upon water content is observed [29,34]. Additionally, water can decrease the solvation ability of organic liquids, thus inhibiting the solvation of impurities and corrosion products. On the other hand, anhydrous ethers cannot form hydrogen bonds, but the small additions of water allow hydrogen bonds to form between the water hydrogen and the ether oxygen. Water added to dimethoxyethane (DME) increases the passive range of steel as shown in Fig. 7 by several hundred millivolts [12] and of iron by contributing to hydrogen bonding or as a Lewis acid [35]. Thus, as stated above, water content needs to be closely monitored and controlled.

The pre-existence of a surface film can affect testing in organic solutions in several ways. In the absence of aggressive species, an air-formed film can be protective even under anodic polarization. Examples of this include iron in propylene carbonate [32,33] and ferritic stainless steel (Fe-18%Cr) in methanol [36]. The presence of competing mechanisms may also contribute to breakdown of metals and alloys in multi-component organic mixtures as observed for steel in PC/DME mixtures [37]. Propylene carbonate interferes with DME electropolymerization by solvating organic cations or cationic radical, or by contaminating the polymer to form pores that allow charge and ionic species to pass through. Adding water to PC-DME mixtures allows the possibility of aqueous passivating mechanisms that further complicate solvent interactions and competition [13]. However, even if aggressive species are present in the solution, the air-formed film may be protective until sufficient anodic polarization is achieved. This creates the need for a testing technique that permits removal of the film enabling examination of the base metal. This can be accomplished by using a stylus to scratch the surface thereby removing any pre-existing protective film to expose new metal. By monitoring the current over time, the corrosion behavior of the material in the absence of any pre-existing film can be observed. The long-term stability of air-formed oxides in organic solutions is not known, and thus the corrosion processes that occur on bared surfaces may be the most relevant to the service conditions. In aqueous solution, cathodic polarization is often used to remove air-formed films. Extensive work in the literature on iron and ferrous alloys [38] as well as other materials [39] support the idea that this approach leads to an oxide-free surface. Such information does not exist for oxide reduction in organic liquids.

However, many workers cathodically polarize their samples before performing electrochemical measurements [28,40-43].

Since the composition and purity of the organic liquid can strongly affect the corrosion process, a key feature to testing is the choice of an appropriate experimental testing solution. This solution should be as close in composition and impurity concentrations to the service solution as possible, unless accelerated testing is desired. The composition of organic liquids can influence the corrosion rate. For example, the corrosion rate of iron in monocarboxylic acids of different chain lengths was studied and showed that as the chain length increased, the corrosion rate decreased [2]. Often organic liquids contain impurities such as water, acids, and metal ions. While these impurities generally have low concentrations in commercially purchased organic liquids, these concentrations could still be significant. For example, nickel in dimethylsulfoxide was only passive when the water concentration was below 100 ppm. Therefore, the testing solution may need to be purified such that the experimental testing solution closely matches the service solution. On the other hand, some corrosion problems develop due to the presence of impurities, so that an initially pure liquid may need to have impurities added to mimic the attack observed. Additionally, if accelerated testing is desired, care should be taken to ensure that the corrosion mechanisms and the location of the corrosion attack (e.g., vapor phase, immersed phase, etc.) accurately mimic in-service observations.

In most organic solutions, the nature of the cathodic process is unclear. In aqueous solutions, water reduction is the most common cathodic reaction, with the reduction of dissolved oxygen also being very important. However, the electrochemical reduction of many organics is very sluggish, and usually poorly characterized. Often the reduction of residual water is assumed to be the predominant cathodic reaction. The role of molecular oxygen on the corrosion process in organic solutions has not been characterized. However, its solubility is nearly ten times higher in methanol than in water [2,44], making it a potentially much more influential oxidant. Additionally, aliphatic ethers are slowly converted to unstable peroxides when in contact with oxygen or air leading to unsafe condition that could induce a violent explosion during distillations [11]. Deaeration by the passage of an inert gas through the solution must be performed with care to avoid the selective evaporation of the liquid. For low boiling point liquids such as methanol, this is of particular importance. For high boiling point liquids such as propylene carbonate, the passage of ultrahigh-purity nitrogen through the solution for extended times can be used to selectively evaporate the water, leading to higher purity solutions, even after the addition of electrolytic salts [33]. The study of solution electrochemistry on platinum can often give insight into the nature of the cathodic as well as anodic reactions.

Temperature affects corrosion testing in organic liquids in that the reaction rates, charge transport diffusional coefficient, and the rate of liquid evaporation are increased and the potential for ignition or explosion is greater. The effect of temperature on reaction kinetics, in general, follows the same principles that hold true for other heterogeneous chemical reactions [2]. Corrosion rates of iron in monocarboxylic acids increase by a factor of 8 to 20 by increasing the temperature from 25 to 80°C. While this behavior is not unique to organic liquids, it is important to realize that deviations in testing temperature compared to service temperature could lead to erroneous conclusions. Elevated temperatures may also lead to alternative reaction pathways leading to other organic intermediate species. Temperature may result in hysteresis in macroscopic polymer

properties such as swelling, elasticity, and turbidity [24]. If testing at elevated temperatures is called for, caution and appropriate safety preparations are needed.

LABORATORY TESTING

Laboratory testing can be of two types: coupon testing and electrochemical testing. This section discusses the special considerations for each type of testing when organic liquids are involved.

Coupon Testing

Exposure of coupons to the solution of interest with post-test evaluation according to accepted standards, such as ASTM G 31, Practice for Laboratory Immersion Corrosion Testing of Metals, is the most directly applicable method of testing in organic liquids. Because of the general lack of data on corrosion in organic liquids, coupon testing often takes on additional importance. While standard test practices have been developed mostly for aqueous solutions, the protocols are essentially independent of the chemical nature of the environment, with minor exceptions. More detailed information on laboratory coupon testing can be found in the relevant chapter of this manual as well as in ASTM G 31. One of the most important caveats for such testing in organic solutions is the need to check that the materials that make up the test apparatus are not affected by the liquid. Many nonmetallics are degraded by or preferentially absorb organic liquids, leading to dimensional and mechanical property changes. If such materials are used as spacers in a coupon exposure rack, unexpected experimental variability can result. For example, the nonmetallics may act as getters for aggressive species, produce aggressive species that would not normally be present, or produce inhibiting agents that bias the results. Compounds that have been used as mounting materials successfully in aqueous solution often do not perform well in either completely organic solutions or in mixed organic/aqueous solutions. Thus, a first step in coupon testing is careful selection of the exposure rack and spacer materials. Often information of this sort is available from the material manufacturer. For example, many nonmetallics have been tested for weight loss/gain and mechanical properties after exposure to a range of different types of organics (e.g., alcohols, aliphatics, aromatics, etc.) at ambient and elevated temperature. While these data can provide general guidance, accelerated tests in the environment of interest may often be warranted.

A second important aspect of laboratory coupon testing in organics is the possibility of an evolution of the solution composition during the test. These changes can be severe, especially at elevated temperatures used to accelerate the corrosion process. Elevated temperature will also accelerate many organic liquid degradation processes, including oxidation by ultraviolet (UV) light. This can be severe in some instances. Thus, it is important to run solution blanks simultaneously. In these tests, no coupon is added to the solution under test, so its composition can be checked both before and after the testing to see if any significant changes in composition have occurred. Degradation reactions for many organics are well-studied and available in the organic chemistry literature. This allows an identification of the by-products expected. Analysis of solutions after the exposure will allow a quantitative measurement of the degradation rate of the liquid in the absence of any interaction with the corroding materials. Comparison of the results with analyses of the

liquid exposed to metal coupons may also give insight into the nature of the cathodic reaction that occurs.

Water ingress during coupon testing must also be monitored if it is suspected that water concentrations are important in the system under study. During testing, seals can develop minute leaks, allowing water levels to increase. Constant purging with an inert gas is an option if the boiling point of the solution is high. For many organics, this is the case. For example, the boiling point of propylene carbonate is over 200°C. However, for low boiling point liquids such as methanol (b.p. = 64.9°C), constant purging will drive off liquid, increasing the concentration of the dissolved, nonvolatile species with time [45].

Electrochemical Testing

For the most part, electrochemical testing in organic solutions is no different than such testing in aqueous solutions. The same experimental arrangements are used, and the appropriate standards, such as ASTM G 5, G 59, and G 61, are still applicable (see section titled Relevant ASTM Standards in this chapter). The chapter in this manual that describes electrochemical testing [4] should be consulted for other information on that subject. This section will focus on the special considerations in electrochemical testing in organic solutions.

The most central difficulty in electrochemical testing of materials in organics is the choice of a suitable reference electrode. Aqueous reference electrodes such as saturated calomel (SCE) have been widely used in such studies, [28,34,36,40,43,45,46], but can suffer from two types of problems. Since these reference electrodes are in contact with the test solution, water can diffuse from the reference electrode into the test solution, thereby changing the concentration of water during the test. The organic liquid will also diffuse into the reference electrode, and may foul the interface, leading to irreversible changes in its potential. Such a change cannot be detected easily, as it would be superimposed on any change in the potential of the working electrode. A second difficulty with using aqueous reference electrodes is the development of a liquid junction potential. This potential develops at the interface of the aqueous solution and the nonaqueous solution due to the large difference in composition. Such potentials are extremely difficult to measure or calculate and vary with time due to the interdiffusion of the two solutions.

Some literature exists on organic liquid-based reference electrodes that have been successfully used in electrochemical studies [47-49]. These include the Ag/AgClO₄(propylene carbonate) [47], Ag/AgCl(methanol) [48], and numerous others as detailed in Ref 49. The Ag/AgClO₄(propylene carbonate) reference electrode developed by Kirowa-Eisner and Gileadi [47] is easy to prepare, stable over time, highly reproducible, and easily stored. This electrode has been used successfully in conducting electrochemical experiments in propylene carbonate solutions. Similarly, the Ag/AgCl(methanol) reference electrode developed by Brossia and Kelly [48], has similar characteristics and has been successfully employed in electrochemical experiments conducted in methanolic solutions. Using a reference electrode where the electrolyte is based upon the testing solution will minimize contamination of the testing solution, fouling of the reference electrode, and the liquid junction potential.

Another aspect of electrochemical testing in organic solutions is the isolation of the counter-electrode from the working electrode. In aqueous solutions this is often ignored since the predominant reactions at the counter-electrode are either oxygen evolution (producing H^+) or hydrogen evolution (producing OH^-) during cathodic and anodic polarization of the working electrode, respectively. Especially in a buffered solution, these reaction products have little effect. However, in an organic solution, the products of the reactions at the counter-electrode are often more complex, and usually unknown. Thus, it is usually good practice to isolate the counter-electrode from the working electrode with porous frits. This will minimize, though not eliminate, any effects of those reaction products.

Relevant ASTM Standards

E 203 Test Method for Water Using Volumetric Karl Fischer Titration

E 1064 Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration

G 1 Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens

G 5 Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements

G 31 Practice for Laboratory Immersion Corrosion Testing of Metals

G 59 Practice for Conducting Potentiodynamic Polarization Resistance Measurements

G 61 Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron, Nickel, or Cobalt-based Alloys

FIELD TESTING

The approach to field studies of corrosion in organic liquids is no different than that used for aqueous corrosion. The choice of coupon size, rack design, test length, and other variables are more strongly influenced by the goals of the testing than by the testing medium. Safety concerns must also be addressed. Different organic liquids have different properties and safety issues, and appropriate references and experts should be consulted. More guidance on the general topic of field testing can be found in the relevant chapter in this manual and in ASTM G 4, Method for Conducting Corrosion Coupon Tests in Plant Equipment. However, the concerns expressed in the section above on laboratory coupon testing with regard to the effects of the organic liquid on the nonmetallic components of the mounting hardware should be considered.

Since the corrosion behavior of materials in organic liquids can be influenced by low levels of water, minimizing the introduction of water from the ambient atmosphere during the introduction of samples or probes should be carefully considered. For long-term testing at sites where there is a constant turnover of solution, these effects may be small for a one-time insertion of

coupons. However, if, for example, a retractable electrochemical probe is used, the solution with which it comes into contact should be flushed in order to allow it to sample the most relevant environment.

In all field testing, the effects of variability in the composition of the stream being studied on the corrosion processes must be considered. Since small changes in the composition in organic solutions can have dramatic effects on the corrosion rate as well as the stability of passive films, large transients in corrosion rate may be experienced. Thus, it is important to complement the corrosion measurements with solution composition measurements in order to develop an understanding of the role of stream composition on the corrosion behavior. Besides ionic composition, water concentrations and the level of liquid by-products should be monitored.

SUMMARY

Corrosion testing in organic liquids has taken on greater importance in recent years due to the increase in the use of nonaqueous and mixed liquids in material and chemical synthesis as well as energy production. While the basic types of corrosion processes are similar in both aqueous and organic liquid environments, special attention must be given to the direct application of testing tools to organic testing due to the complexity of organic systems. The wide variety of organic liquids and mixtures increases the number of experimental variables that need to be considered and controlled.

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Captions:

Table 1 – Weight loss of aluminum in organic acids versus acid concentration [4].

FIG. 1—Comparison of electrolyte conductivity (S/m) of various liquids with HCl added as a supporting electrolyte [4].

FIG. 2—Increase in water content in methanol due to absorption from ambient atmosphere [7].

FIG. 3—Corrosion rate (mm/yr) of iron in monocarboxylic acids of different chain lengths (formic acid, acetic acid, propionic acid, butyric acid) [2].

FIG. 4—Normal electrode potentials of metals in different liquids on the ferrocene/ferricinium⁺ scale at 25°C [2].

FIG. 5—The effect of water content on the anodic polarization behavior of nickel in methanol containing 1 M H₂SO₄ [29].

FIG. 6—The effect of water content on the anodic polarization of iron in propylene carbonate at 25°C [33].

FIG. 7 – The effect of water content on the anodic polarization of carbon steel in dimethoxyethane at 25°C [12].

TABLE 1—Weight loss of aluminum in organic acids versus acid concentration [10].

Acid	Acid Concentration, % (Remainder Water)	Mass Loss, g/m ² day
Acetic	99.5	0.4
Acetic	99.94	990.0
Propionic	99.5	2.0
Propionic	99.8	2650

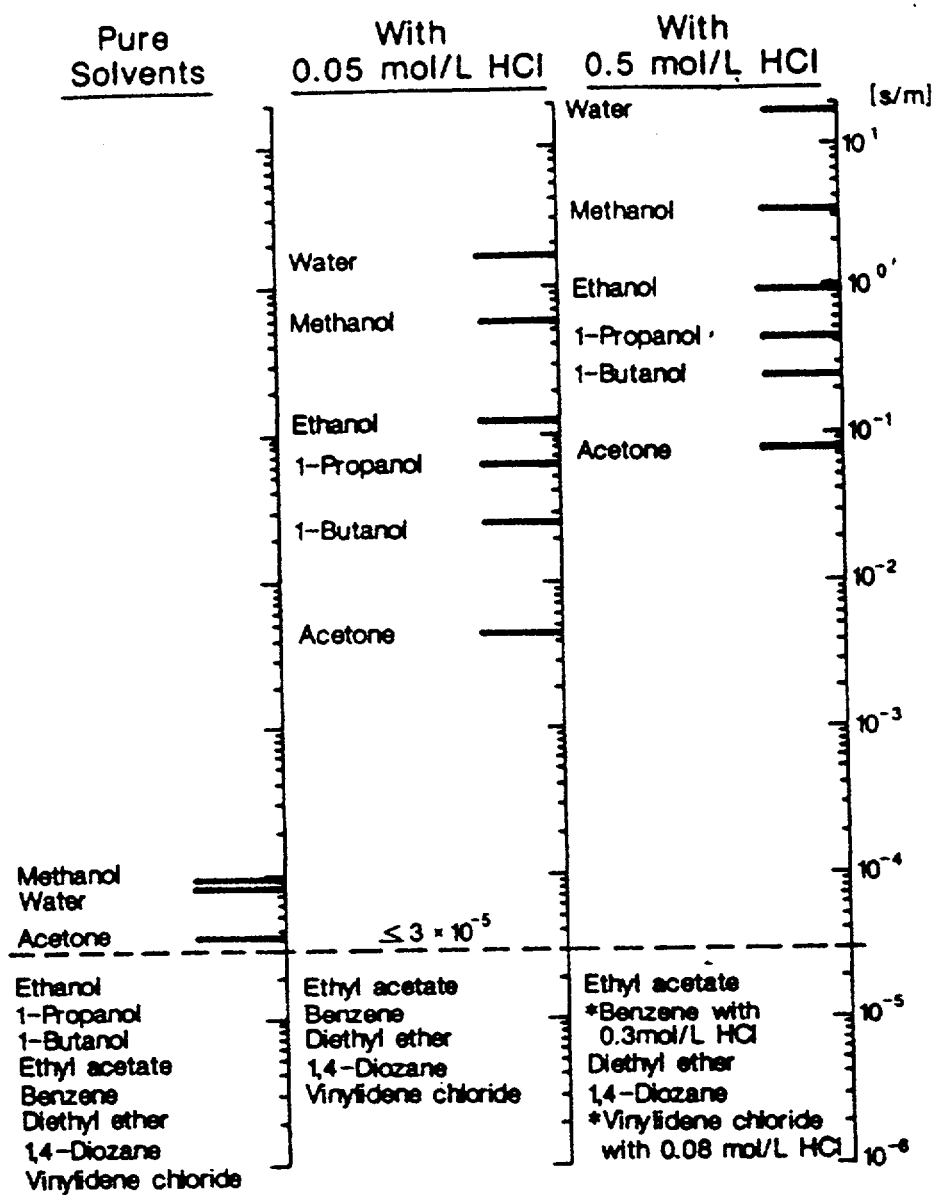


FIG. 1—Comparison of electrolyte conductivity (S/m) of various liquids with HCl added as a supporting electrolyte [2].

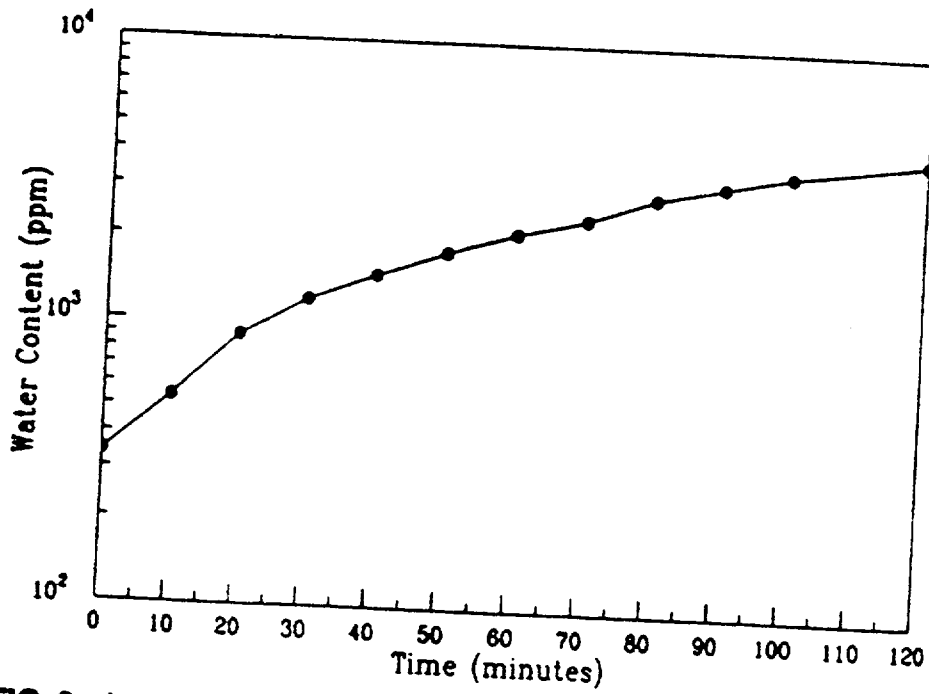


FIG. 2—Increase in water content in methanol due to absorption from ambient atmosphere [5].

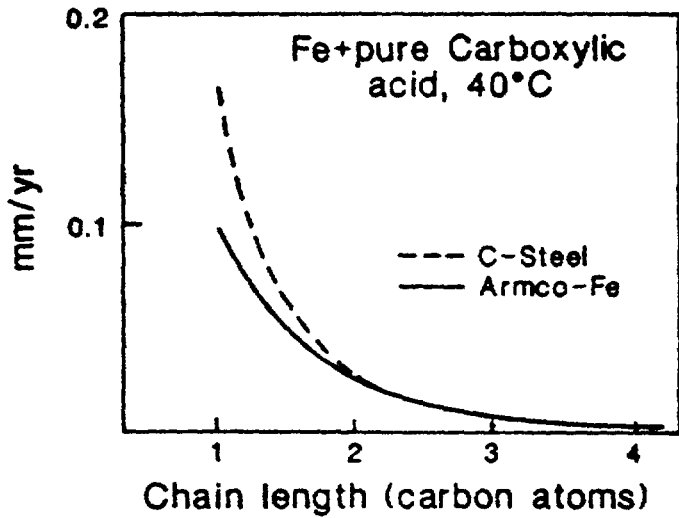


FIG. 3—Corrosion rate (mm/yr) of iron in monocarboxylic acids of different chain lengths (formic acid, acetic acid, propionic acid, butyric acid) [1].

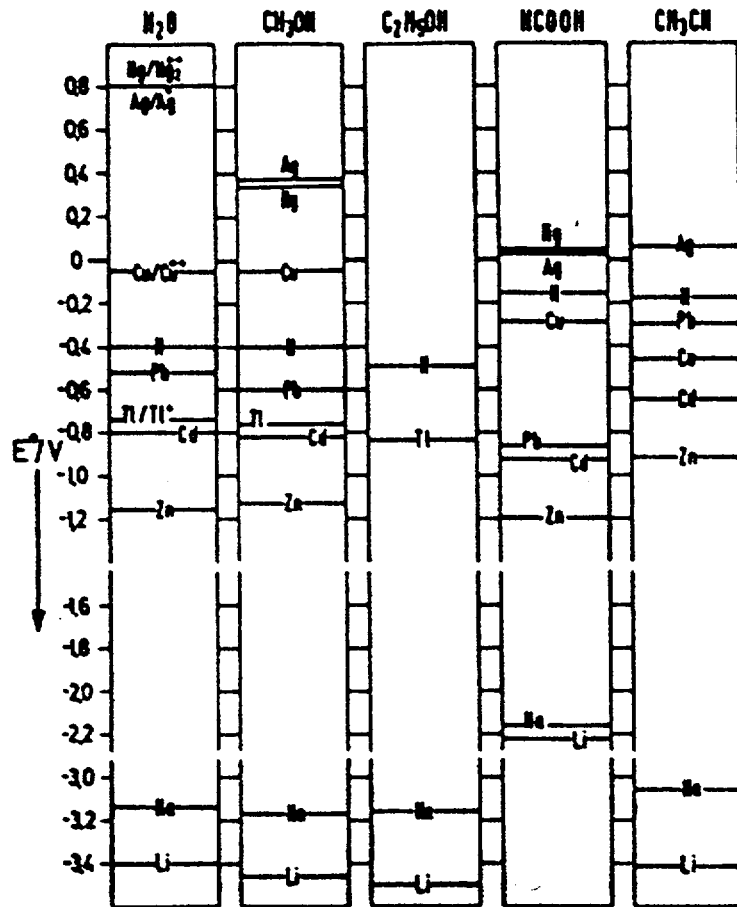
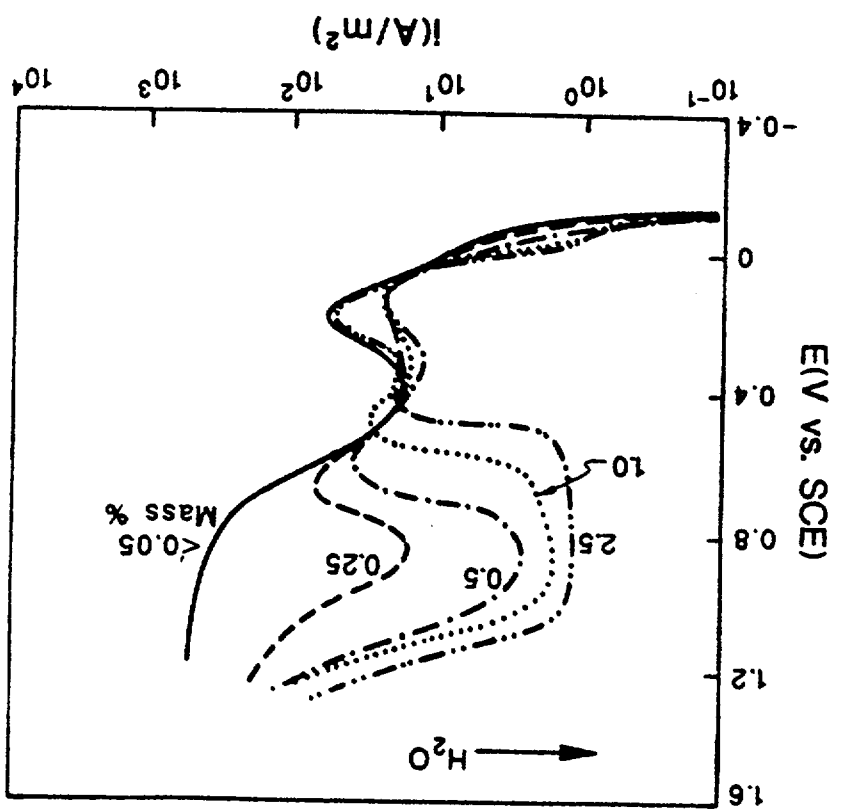


FIG. 4—Normal electrode potentials of metals in different liquids on the ferrocene/ferricinium⁺ scale at 25°C [7].

FIG. 5—The effect of water content on the anodic polarization behavior of nickel in methanol containing 1 M H_2SO_4 [12].



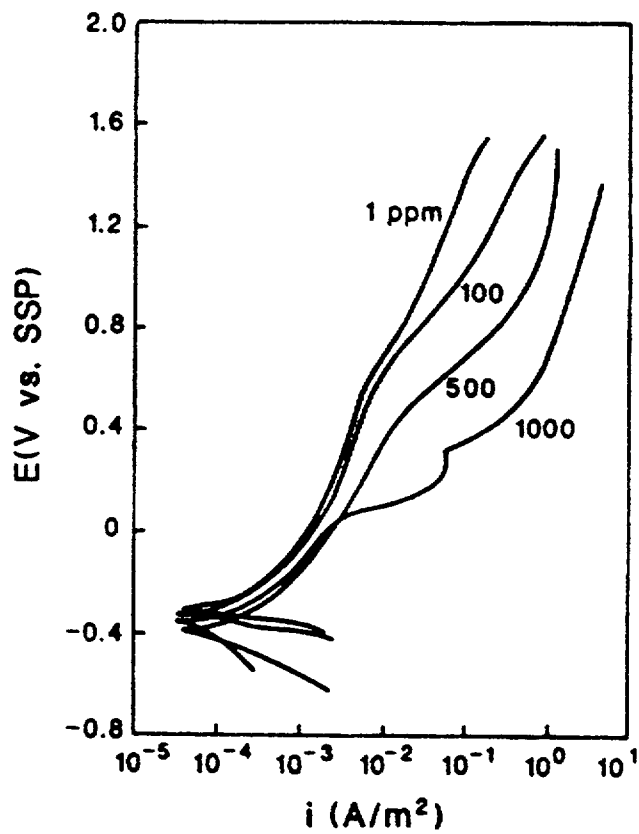


FIG. 6—The effect of water content on the anodic polarization of iron in propylene carbonate at 25°C [16].

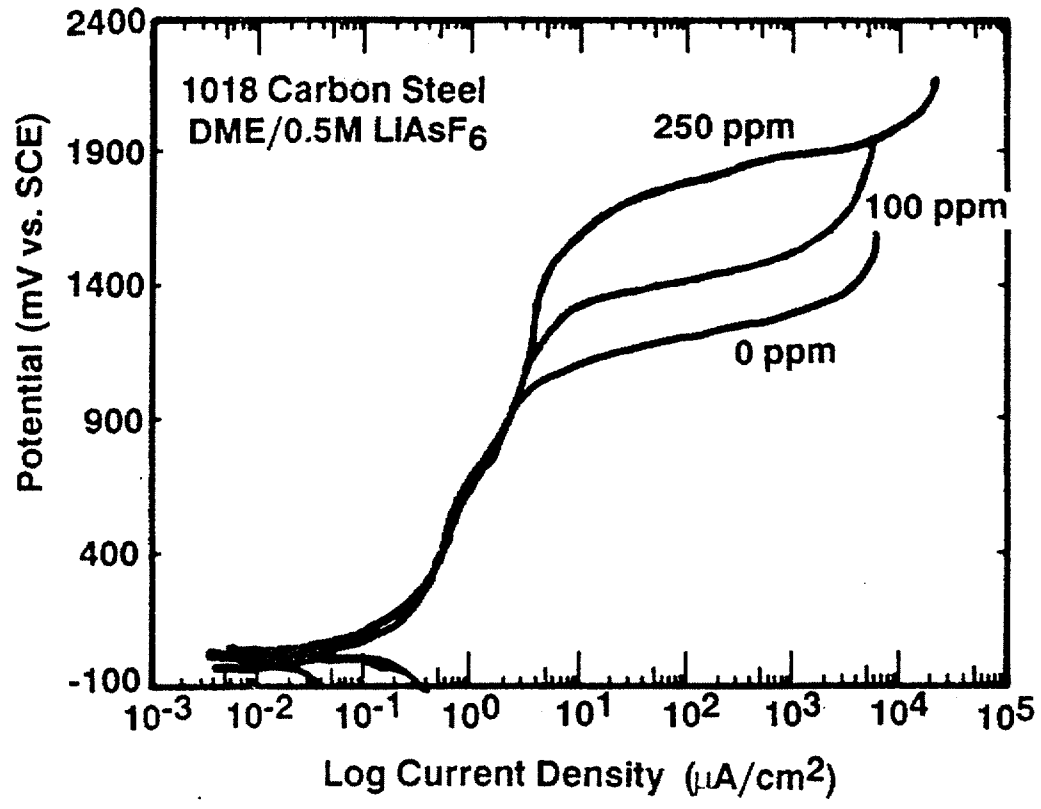


Figure 7